The existence of a $^2\mathrm{P}^o$ excited state for the e^+Ca system

M.W.J.Bromley[*]

Department of Physics, San Diego State University, San Diego CA 92182, USA

J.Mitroy[†]

Faculty of Technology, Charles Darwin University, Darwin NT 0909, Australia

(Dated: February 2, 2008)

The Configuration Interaction method is used to demonstrate that there is an electronically stable state of positronic calcium with an orbital angular momentum of $L = 1$. This prediction relies on the use of an asymptotic series to estimate the variational limit of the energy. The best estimate of the binding energy is 37 meV. A discussion of the structure of the system is also presented.

In 1997 the existence of positron-atom bound states was demonstrated by two independent calculations [1, 2] of the e^+Li ground state. Subsequently, it has been shown that at least nine other atoms can attach a positron and form an electronically stable bound state [3]. Besides its intrinsic interest, the knowledge that positrons can form bound states has been crucial to recent developments in understanding the very large annihilation rates that occur when positrons annihilate with various molecules in the gas phase [4, 5, 6, 7]. The problem of explaining the large annihilation rates had remained essentially unresolved almost since the first experiments [8, 9, 10]. While the possible influence of bound states upon the annihilation rate had been conjectured [11, 12], the lack of hard evidence for the existence of positron-atom bound states had certainly inhibited development of compound state models of positron-molecule annihilation [12, 13, 14, 15]. The prevailing view on positron binding [16] has changed to such an extent over the last decade that a positron-atom (or positron-molecule) interaction potential that supports a positron bound state can now be regarded as mundane [17].

One feature of the atomic calculations is that binding has only been seen for spherically symmetric states. The angular momentum of the parent atom ground state and the positron-atom composite state are always zero [3]. Another feature is that binding occurs to atoms with an ionization energy close to 6.80 eV (the Ps binding energy) and the binding energies are largest for atoms with their ionization energies closest to 6.80 eV [3].

While the existence of positron binding to atoms (and molecules) is now accepted, the question of whether these complexes have excited states is largely unexplored. Whether such states exist is best determined by calculations that are sufficiently sophisticated to accurately model the delicate interplay of attractive and repulsive coulomb interactions with the additional complication of an angular momentum barrier. (We note the prediction of a $^2\mathrm{P}^o$ state of e^+Mg by Gribakin *et al* [18]. However, the many body theory of Gribakin *et al* is known to grossly overestimate the strength of the positron-atom interaction [3, 19, 20, 21] and so the result has never been taken seriously.) First, it is necessary to identify what is meant by an excited state. The states of interest should have the same long-range dissociation channel as the lower lying positronic atom ground state. This is to distinguish these systems from states which are better described as a positron bound to an excited state of the atom (an example is the metastable e^+He($^3\mathrm{S}^e$) state [22]).

The present letter describes some very large configuration interaction (CI) calculations of the e^+Ca system that indicate the presence of a $^2\mathrm{P}^o$ state with a binding energy of ≈ 37 meV with respect to the lowest energy $\mathrm{Ca}^+(4s)$ + Ps($1s$) dissociation channel (the ionization energy of the Ca atom is less than 6.80 eV). This system is the first representative of a new class of positron-atom bound states whose existence is more surprising than that of the Ca^- $^2\mathrm{P}^o$ negative ion [23, 24].

The CI method as applied to positron-atom systems with two valence electrons and a positron has been discussed previously [20, 25, 26], but a short description is worthwhile. The model Hamiltonian is initially based on a Hartree-Fock (HF) wave function for the neutral atom ground state. One- and two-body semi-empirical polarization potentials are added to the potential field of the HF frozen-core and the parameters of the core-polarization potentials defined by reference to the spectrum of Ca^+ [20]. The effective Hamiltonian for the system with 2 valence electrons and a positron was

$$
\begin{aligned}
H \;=\; & -\frac{1}{2}\nabla_0^2 - \sum_{i=1}^{2}\frac{1}{2}\nabla_i^2 - V_{\mathrm{dir}}(\mathbf{r}_0) + V_{\mathrm{p1}}(\mathbf{r}_0) \\
& + \sum_{i=1}^{2}\left(V_{\mathrm{dir}}(\mathbf{r}_i) + V_{\mathrm{exc}}(\mathbf{r}_i) + V_{\mathrm{p1}}(\mathbf{r}_i)\right) - \sum_{i=1}^{2}\frac{1}{r_{i0}} \\
& + \sum_{i<j}^{2}\frac{1}{r_{ij}} - \sum_{i<j}^{2}V_{\mathrm{p2}}(\mathbf{r}_i,\mathbf{r}_j) + \sum_{i=1}^{2}V_{\mathrm{p2}}(\mathbf{r}_i,\mathbf{r}_0) \; . \quad (1)
\end{aligned}
$$

The direct potential (V_{dir}) represents the interaction with

the HF $1s^2 2s^2 2p^6 3s^2 3p^6$ electron core. The direct part of the core potential is attractive for electrons and repulsive for the positron. The exchange potential (V_{exc}) between the valence electrons and the HF core was computed without approximation.

The one-body polarization potential (V_{p1}) was a semi-empirical polarization potential with the functional form

$$V_{\text{p1}}(r) = -\sum_{\ell m} \frac{\alpha_d g_\ell^2(r)}{2r^4} |\ell m\rangle\langle \ell m|. \qquad (2)$$

The factor α_d is the static dipole polarizability of the core and $g_\ell^2(r) = 1 - \exp\left(-r^6/\rho_\ell^6\right)$ is a cutoff function designed to make the polarization potential finite at the origin. The core dipole polarizability was set to 3.16 a_0^3 while the ρ_ℓ were adjusted to reproduce the Ca$^+$ spectrum [20] (the Ca$^+$ energy is -0.43628653 Hartree in the model potential while experiment gives -0.436278 Hartree [27]). The same cutoff function has been adopted for both the positron and electrons. The two-body polarization potential (V_{p2}) is defined as

$$V_{\text{p2}}(\mathbf{r}_i, \mathbf{r}_j) = \frac{\alpha_d}{r_i^3 r_j^3} (\mathbf{r}_i \cdot \mathbf{r}_j) g_{\text{p2}}(r_i) g_{\text{p2}}(r_j) . \qquad (3)$$

where $g_{\text{p2}}(r)$ is chosen to have a cutoff parameter obtained by averaging the ρ_ℓ. This model has been used to describe the calcium spectrum to quite high accuracy [20, 28].

The CI basis was constructed by letting the two electrons and the positron form all the possible total angular momentum $L_T = 1$ configurations, with the two electrons in a spin-singlet state, subject to the selection rules,

$$\max(\ell_0, \ell_1, \ell_2) \leq J , \qquad (4)$$
$$\min(\ell_1, \ell_2) \leq L_{\text{int}} , \qquad (5)$$
$$(-1)^{(\ell_0 + \ell_1 + \ell_2)} = -1 . \qquad (6)$$

In these rules ℓ_0, ℓ_1 and ℓ_2 are respectively the orbital angular momenta of the positron and the two electrons. We define $\langle E\rangle_J$ to be the energy of the calculation with a maximum orbital angular momentum of J.

The two-electron-positron calculations with non-zero total angular momentum were first validated against the previous $L_T = 1$ PsH calculations of Tachikawa [29]. Using their Gaussian-type orbitals we reproduced their reported energy and annihilation rates (note that the PsH states with $L_T > 0$ are unbound).

The Hamiltonian for the e^+Ca ^{2}P^o state was diagonalized in a CI basis constructed from a very large number of single particle orbitals, including orbitals up to $\ell = 14$. There was a minimum of 14 radial basis functions for each ℓ. The largest calculation was performed with $J = 14$ and $L_{\text{int}} = 3$ and gave a CI basis dimension of 874888. The parameter L_{int} does not have to be particularly large

TABLE I: Results of CI calculations for the e^+Ca ^{2}P^o state as a function of J, and for $L_{\text{int}} = 3$. The total number of configurations is denoted by N_{CI}. The 3-body energy of the state, relative to the energy of the Ca^{2+} core, is given in Hartree. The threshold for binding is -0.68628653 Hartree, and ε gives the binding energy (in Hartree) against dissociation into Ps + Ca$^+(4s)$. The values of $\langle E\rangle_\infty$ were determined at $J = 14$.

J	N_{CI}	$\langle E\rangle_J$	ε_J
1	10094	-0.64319380	-0.04309273
2	34244	-0.64976077	-0.03652576
3	79198	-0.65519252	-0.03109401
4	140168	-0.66104645	-0.02524009
5	206822	-0.66626528	-0.02002126
6	278754	-0.67046020	-0.01582633
7	352156	-0.67372823	-0.01255830
8	426832	-0.67626613	-0.01002041
9	501508	-0.67824946	-0.00803707
10	576184	-0.67981518	-0.00647135
11	650860	-0.68106444	-0.00522209
12	725536	-0.68207134	-0.00421520
13	800212	-0.68289035	-0.00339618
14	874888	-0.68356185	-0.00272468
		$\langle E\rangle_\infty$	ε_∞
1-term eq.(7)		-0.68648706	0.0002005
2-term eq.(7)		-0.68739784	0.0011113
3-term eq.(7)		-0.68763826	0.0013517

since it is mainly concerned with electron-electron correlations [20]. The resulting Hamiltonian matrix was diagonalized with the Davidson algorithm [30], and a total of 4000 iterations were required for the largest calculation.

The energy of the e^+Ca ^{2}P^o state as a function of J is given in Table I. The binding energy is defined as $\varepsilon = -(0.68628653 + E)$. None of the calculations give an energy lower than the Ca$^+(4s)$ + Ps($1s$) threshold. The main technical problem afflicting CI calculations of positron-atom interactions is the slow convergence of the energy with J [3, 26, 31, 32] and the present calculation is no exception to the rule. One way to determine the $J \to \infty$ energy, $\langle E\rangle_\infty$, is to make use of an asymptotic analysis. It has been shown that successive increments, $\Delta E_J = \langle E\rangle_J - \langle E\rangle_{J-1}$, to the energy can written as an inverse power series [26, 33, 34, 35, 36], viz

$$\Delta E_J \approx \frac{A_E}{(J + \frac{1}{2})^4} + \frac{B_E}{(J + \frac{1}{2})^5} + \frac{C_E}{(J + \frac{1}{2})^6} + \cdots . \qquad (7)$$

The $J \to \infty$ limit, has been determined by fitting sets of $\langle E\rangle_J$ values to asymptotic series with either 1, 2 or 3 terms. The coefficients, A_E, B_E and C_E for the 3-term expansion are determined at a particular J from 4 successive energies ($\langle E\rangle_{J-3}$, $\langle E\rangle_{J-2}$, $\langle E\rangle_{J-1}$ and $\langle E\rangle_J$). Once the coefficients have been determined it is easy to sum the series to ∞ and obtain the variational limit.

Application of asymptotic series analysis to helium has resulted in CI calculations reproducing the ground state energy to an accuracy of $\approx 10^{-8}$ Hartree [36, 37]. Figure 1 shows the estimates of $\langle E \rangle_\infty$ as a function of J.
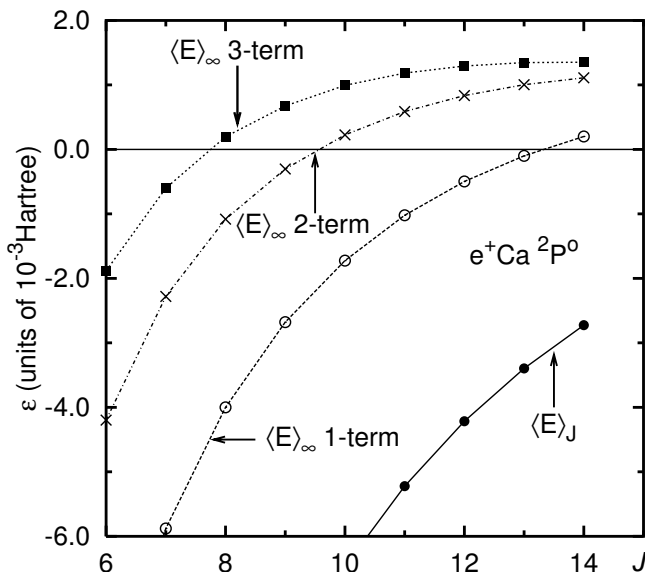

FIG. 1: The binding energy (in units of Hartree) of the $^2P^o$ state of e^+Ca as a function of J. The directly calculated energy is shown as the solid line while the $J \to \infty$ limits using eq. (7) with 1, 2 or 3 terms are shown as the dashed lines. The Ca$^+(4s)$ + Ps$(1s)$ dissociation threshold is shown as the horizontal solid line.

The different extrapolations all give energies below the dissociation threshold and indicate that the e^+Ca $^2P^o$ state is electronically stable. The energy of the three-term extrapolation does seem to have stabilized at a binding energy of ≈ 0.00135 Hartree (37 meV). The two-term binding energy is slightly smaller but does seem to be approaching the three-term estimate. The one-term estimate of $\langle E \rangle_\infty$ is also bound, although its binding energy is smaller. The precise estimates of $\langle E \rangle_\infty$ evaluated at $J = 14$ are given in Table I.

Since the binding energy is small it is desirable to examine the areas of uncertainty in the model and computation to determine whether they could invalidate the prediction.

The interaction between the core and valence electrons was tested quite simply by adjusting the core polarizability by $\pm 5\%$ (leading to a change of $\pm 0.16\%$ in the neutral Ca ionization energy). When this was done, the overall change in the e^+Ca $^2P^o$ binding energy at $J = 14$ was ± 0.00013 Hartree, i.e. $\pm 10\%$ of the final binding energy.

Choosing the polarization potential cutoff function for the positron to be the same as the electron will lead to the binding energy being underestimated. First, it is known from calculations on the rare gases that the positron po-

larization potential is more attractive than the equivalent electron potential [38, 39, 40]. Also, the *ab-initio* calculations on the small systems, e^+He$(^3S^e)$ and e^+Li have given larger binding energies (by 1-2%) than calculations using model potentials to represent the core [41, 42].

The lack of completeness in the finite dimension radial basis is also not an issue. Computational investigations have revealed that accurate prediction of the ΔE_J energy increments requires a larger basis as J increases [26, 36]. This results in the typical CI partial wave expansion with a fixed dimension radial basis for the different ℓ-values having an inherent tendency to underestimate the binding energy [26, 36].

Finally, a computational null experiment was performed on the PsH system. This system does not have a $^2P^o$ bound state. A calculation of almost identical size to the e^+Ca system was performed. An unbound system would be expected to have an $\langle E \rangle_\infty$ that asymptotes to the threshold energy, or to a value above threshold, and this is what is seen to occur in Figure 2.
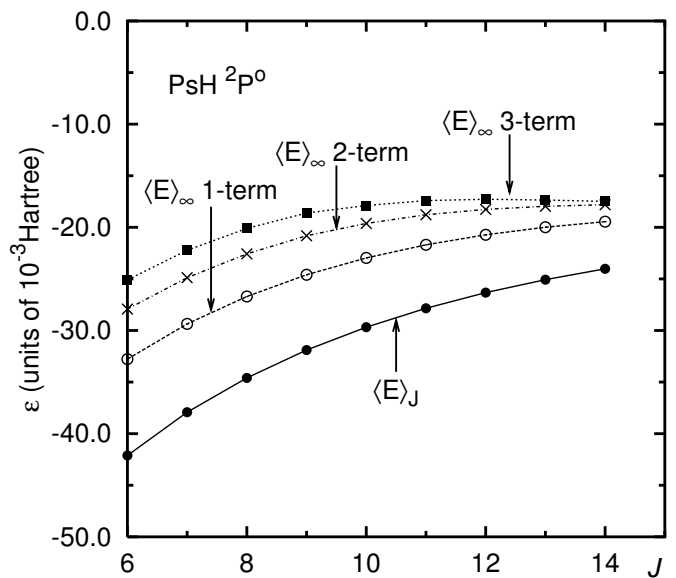

FIG. 2: The binding energy, $\varepsilon = -(0.75 + E)$, of the PsH $^2P^o$ system as a function of J. The directly calculated energy is shown as the solid line while the $\langle E \rangle_\infty$ limits using eq. (7) are shown as the dashed lines.

A e^+Ca valence annihilation rate of $\Gamma = 1.42 \times 10^9$ sec^{-1} has also been determined using an asymptotic analysis similar to that used for the energy [21, 26]. This large annihilation rate suggests that a large fraction of the wave function consists of a Ca$^+$+Ps$(1s)$ cluster [3].

The system is compact despite its small binding energy and the mean positron radius for a converged calculation was estimated at $\langle r_p \rangle \approx 8.7$ a_0. The e^+Ca ground state with a binding energy 14 times larger has almost the same $\langle r_p \rangle$ [21]. However, the large r form of the $^2P^o$

wave function must have a Ca$^+$(4s) + Ps(1s) structure with the Ps(1s) center of mass being in an $L = 1$ state with respect to the residual ion. The centrifugal barrier associated with the non-zero angular momentum acts to confine the positron probability distribution.

The present calculations indicate that positronic calcium has a ^{2}P^o excited state. The existence of both ^{2}S^e and ^{2}P^o states of e^+Ca makes optical detection a possibility. While the present calculation does not present an absolute variational proof of binding (the calculation would have to be extended to $J \approx 20$ for this to occur), the evidence in support of the excited state is strong. It is worth noting that extrapolating finite dimension basis sets to the variational limit is quite common in the field of quantum chemistry [43].

One consequence of this result lies in the area of positron annihilation. It has been shown that a low energy p-wave shape resonance can lead to very large values of $Z_{\rm eff}$ [44]. It is possible for thermally averaged values of $Z_{\rm eff}$ to exceed 10^4 since the energy dependence of $Z_{\rm eff}$ for a p-wave shape resonance is reasonably compatible with a Maxwell-Boltzmann energy distribution. The existence of p-wave shape resonances are certainly plausible given the existence of the ^{2}P^o bound state and provides another reaction that can contribute to the very large annihilation rates seen in gas-phase experiments [4, 8, 9, 10]. And very recently, $Z_{\rm eff}$ peaks in the annihilation spectra for dodecane (C$_{12}$H$_{26}$) and tetradecane (C$_{14}$H$_{30}$) have been tentatively identified as a positronically excited bound state associated with the C-H stretch mode [45, 46].

---

* Electronic address: mbromley@physics.sdsu.edu

† Electronic address: jxm107@rsphysse.anu.edu.au

[1] G. G. Ryzhikh and J. Mitroy, Phys. Rev. Lett. **79**, 4124 (1997).

[2] K. Strasburger and H. Chojnacki, J. Chem. Phys. **108**, 3218 (1998).

[3] J. Mitroy, M. W. J. Bromley, and G. G. Ryzhikh, J. Phys. B **35**, R81 (2002).

[4] K. Iwata, G. F. Gribakin, R. G. Greaves, C. Kurz, and C. M. Surko, Phys. Rev. A **61**, 022719 (2000).

[5] S. J. Gilbert, L. D. Barnes, J. P. Sullivan, and C. M. Surko, Phys. Rev. Lett. **88**, 043201 (2002).

[6] J. Mitroy, Physics World **15**, 24 (2002).

[7] J. P. Marler, L. D. Barnes, S. J. Gilbert, J. P. Sullivan, J. A. Young, and C. M. Surko, Nucl. Instrum. Methods Phys. Res. B **221**, 84 (2004).

[8] D. A. L. Paul and L. Saint-Pierre, Phys. Rev. Lett. **11**, 493 (1963).

[9] M. Charlton, Rep. Prog. Phys. **48**, 737 (1985).

[10] C. M. Surko, A. Passner, M. Leventhal, and F. J. Wysocki, Phys. Rev. Lett. **61**, 1831 (1988).

[11] V. I. Goldanskii and Y. S. Sayasov, Phys. Lett. **13**, 300 (1964).

[12] V. A. Dzuba, V. V. Flambaum, G. F. Gribakin, and W. A. King, J. Phys. B **29**, 3151 (1996).

[13] L. D. Barnes, S. J. Gilbert, and C. M. Surko, Phys. Rev. A **67**, 032706 (2003).

[14] G. F. Gribakin, Phys. Rev. A **61**, 022720 (2000).

[15] E. S. Reich, New Scientist **April 24**, 34 (2004).

[16] D. M. Schrader, Nucl. Instrum. Methods Phys. Res. B **143**, 209 (1998).

[17] T. Nishimura and F. A. Gianturco, Europhys. Lett. **68**, 377 (2004).

[18] G. F. Gribakin and W. A. King, Can. J. Phys. **74**, 449 (1996).

[19] J. Mitroy and G. G. Ryzhikh, J. Phys. B **34**, 2001 (2001).

[20] M. W. J. Bromley and J. Mitroy, Phys. Rev. A **65**, 062505 (2002).

[21] M. W. J. Bromley and J. Mitroy, Phys. Rev. A **73**, 032507 (2006).

[22] G. G. Ryzhikh and J. Mitroy, J. Phys. B **31**, 3465 (1998).

[23] D. J. Pegg, J. S. Thompson, R. N. Compton, and G. D. Alton, Phys. Rev. Lett. **59**, 2267 (1987).

[24] C. F. Fischer, J. B. Lagowski, and S. H. Vosko, Phys. Rev. Lett. **59**, 2263 (1987).

[25] M. W. J. Bromley and J. Mitroy, Phys. Rev. A **65**, 012505 (2002).

[26] J. Mitroy and M. W. J. Bromley, Phys. Rev. A **73**, 052712 (2006).

[27] S. Bashkin and J. O. Stoner, *Atomic Energy Levels and Grotrian Diagrams* (North Holland, Amsterdam, 1975), vol. I.

[28] J. Mitroy and M. W. J. Bromley, Phys. Rev. A **68**, 052714 (2003).

[29] M. Tachikawa, Chem. Phys. Lett. **350**, 269 (2001).

[30] A. Stathopolous and C. Froese Fischer, Comput. Phys. Commun. **79**, 268 (1994).

[31] J. Mitroy and G. G. Ryzhikh, J. Phys. B **32**, 2831 (1999).

[32] V. A. Dzuba, V. V. Flambaum, G. F. Gribakin, and C. Harabati, Phys. Rev. A **60**, 3641 (1999).

[33] C. Schwartz, Phys. Rev. **126**, 1015 (1962).

[34] D. P. Carroll, H. J. Silverstone, and R. P. Metzger, J. Chem. Phys. **71**, 4142 (1979).

[35] R. N. Hill, J. Chem. Phys. **83**, 1173 (1985).

[36] M. W. J. Bromley and J. Mitroy, Int. J. Quantum Chem. p. in press (2006).

[37] S. Salomonsen and P. Oster, Phys. Rev. A **40**, 5559 (1989).

[38] J. Mitroy and I. A. Ivanov, Phys. Rev. A **65**, 012509 (2002).

[39] J. Mitroy and M. W. J. Bromley, J.Phys. B **36**, 793 (2003).

[40] J. Mitroy and M. W. J. Bromley, Phys. Rev. A **67**, 034502 (2003).

[41] J. Mitroy, Phys. Rev. A **72**, 032503 (2005).

[42] J. Mitroy, Phys. Rev. A **70**, 024502 (2004).

[43] W. Klopper, K. L. Bak, P. Jorgensen, J. Olsen, and T. Helgaker, J. Phys. B **32**, R103 (1999).

[44] M. W. J. Bromley and J. Mitroy, Phys. Rev. A **67**, 062709 (2003).

[45] L. D. Barnes, J. A. Young, and C. M. Surko, Phys. Rev. A **74**, 012706 (2006).

[46] G. F. Gribakin and C. M. R. Lee, Nucl. Instrum. Methods Phys. Res. B **247**, 31 (2006).